Magnetic Susceptibilities of Coronene, Pentacene and Related Compounds

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Introduction

In a previous paper[1] the magnetic susceptibilities and anisotropies of polycyclic aromatic compounds have been presented. In that paper, however, data on coronene and pentacene have not been included. Recently, good specimens of these compounds have kindly been provided by Dr. E. Clar of the University of Glasgow, who had synthesized them. We append here the data on these compounds with some related ones which have been re-examined.

Experimental and Results

The measurements of the magnetic susceptibility were made by the Gouy method, referring to the volume susceptibility of water as $-0.720\cdot10^{-6}$ at 20°C.

Coronene.—Coronene which has been provided by Dr. Clar consists of long yellow needle crystals.

The gram susceptibility, $-\chi\cdot10^6=0.810\pm0.003$ (in c.g.s. unit).

The mole susceptibility, $-\chi_M\cdot10^6=243.3$.

Pentacene.—The pentacene which has been provided by Dr. Clar is a deep bluish violet powder. After preliminary measurements had been made, the sample was sublimed in vacuum. The greater part of the sample was sublimed excepting a small amount of dark residue. In practice, however, this procedure had not much effect upon the result.

The gram susceptibility, $-\chi\cdot10^6=0.738\pm0.003$.

The mole susceptibility, $-\chi_M\cdot10^6=205.4$.

Anthracene and Tetracene.—Anthracene was synthesized starting from anthraquinone, and tetracene was obtained from Fulka. They were purified carefully in the usual manner.

Anthracene, $-\chi\cdot10^6=0.731\pm0.002$.

Tetracene, $-\chi\cdot10^6=0.736\pm0.002$.

Violanthrene.—The magnetic susceptibility of violanthrene has been re-examined, because there occured some doubt about the purity of the former specimen. Violanthrone was synthesized from benzanthrone, and reduced to violanthrene by zinc dust fusion after Clar. In this procedure, the so-called B-compound was carefully separated. The specimen was purified by sublimation in vacuum.

The gram susceptibility, $-\chi\cdot10^6=0.733\pm0.004$.

The mole susceptibility, $-\chi_M\cdot10^6=312.6$.

Discussion

Let K_1, K_2 and K_3 be the principal mole susceptibilities of the molecule, where K_1 and K_2 are those in the plane of molecule and K_3 is that perpendicular to it. As presented in the previous paper, K_1 $(=K_2)$ is calculated by the empirical formula after Hazato[2],

$$K_1=\Sigma\chi(C=)+\Sigma\chi(H) \qquad (1)$$

where $\chi(C=)=-3.36\cdot10^{-6}$ and $\chi(H)=-2.93\cdot10^{-6}$. The diamagnetic anisotropy is given by

$$\varDelta K=K_3-K_1=3(\chi_M-K_1) \qquad (2)$$

This results for coronene, $K_1=-115.8\cdot10^{-6}$, and $\varDelta K=-383\cdot10^{-6}$.

Such an approximate calculation has, hitherto, been made because it is difficult to obtain single crystals large enough in size for the magnetic measurements.

For coronene, however, Rogers[3] has measured the magnetic anisotropy of a single crystal, and his results were,

$$X_1-X_2=180\cdot10^{-6},\quad X_1-X_3=210\cdot10^{-6},$$
$$X_2-X_3=30\cdot10^{-6},\ \text{and}\ \varDelta K=-390\cdot10^{-6},$$

where X_1, X_2 and X_3 are the principal mole susceptibilities of the crystal. However, the mean susceptibility has not been measured but was assumed to be $\chi_M=-220\cdot10^{-6}$ following Pascal's formula. This value is somewhat small from the present view. When we combine the observed value of χ_M $(=-243\cdot10^{-6})$ with his data of anisotropy, we obtain

$$-X_1\cdot10^6=113,\quad -X_2\cdot10^6=293,\quad \text{and}$$
$$-X_3\cdot10^6=323.$$

As coronene crystal belongs to monoclinic system, X_1 is equal to K_1[4]. Consequently, this value of X_1 (or K_1) as well as $\varDelta K$ are in good agreement with the corresponding values which are obtained using equation (1).

Krishnan and Banerjee[5] have observed the mean susceptibilities and the anisotropies of single crystals of chrysene, pyrene and perylene. Their results are compared with the

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[1] H. Akamatu and Y. Matsunaga, This Bulletin, 26, 364 (1953).

[2] H. Shiba and G. Hazato, This Bulletin, 22, 92 (1949).

[3] M.T. Rogers, *J. Am. Chem. Soc.*, **69**, 1506 (1947).

[4] K. Lonsdale and K.S. Krishnan, *Proc. Roy. Soc., London*, **A156**, 597 (1936).

[5] a. K.S. Krishnan and S. Banerjee, *Phil. Trans. Roy. Soc.*, **A234**, 265 (1935). b. S. Banerjee, *Z. Krist.*, **100**, 316 (1939).

corresponding ones which were calculated in accordance with the equation (1) using our own observed values of mean susceptibility.

Chrysene:	(K. & B.) $-\chi_M\cdot10^6=160.7$,	$-K_1\cdot10^6=$ 88.0,	$-\Delta K\cdot10^6=218$.
	(A. & M.) 168.5,	95.6,	219.
Pyrene:	(K. & B.) $-\chi_M\cdot10^6=154.9$,	$-K_1\cdot10^6=$ 80.6,	$-\Delta K\cdot10^6=223$.
	(A. & M.) 148.6,	83.1,	197.
Perylene:	(B.) $-\chi_M\cdot10^6=159.6$,	$-K_1\cdot10^6=$ 95.5,	$-\Delta K\cdot10^6=192$.
	(A. & M.) 166.8,	102.4,	193.

They are in pretty good agreement with each other, therefore, an empirical formula such as equation (1) is a useful expression.

There is a little argument about the contribution of the number of aromatic rings to the diamagnetic anisotropy of the polycyclic hydrocarbon molecule. In the present case of coronene, $\Delta K/\Delta K_B=7.2$, where ΔK_B, the diamagnetic anisotropy of benzene, is $-54\cdot10^{-6}$. This value denotes approximately the number of aromatic rings in coronene molecule, whilst, the theoretical calculation by the molecular orbital method after London has been presented as

$\Delta K/\Delta K_B=9.796$ (when $S=0$),
and $\Delta K/\Delta K_B=10.13$ (when $S=0.25$),

where S is the overlap integral[6]. The present result reveals that these calculated values are too large.

Assuming $\Delta K=-(\mathrm{Ne}^2/4\,\mathrm{mc}^2)\sum_p\bar{r}^2$, where p is the number of π-electrons and other symbols are the usual ones, the average effective radius of the π-electron orbitals $\sqrt{\bar{r}^2}$ has been estimated. The result is $\sqrt{\bar{r}^2}=1.94$ Å for coronene. Such a quantity is assumed as measuring the delocalized character of π-electrons in a molecule and increases linearly with the number of π-electrons in a series of hydrocarbons. This is shown in Fig. 1. This figure includes also the re-examined value for violanthrene i.e., $\sqrt{\bar{r}^2}=1.74$ Å.

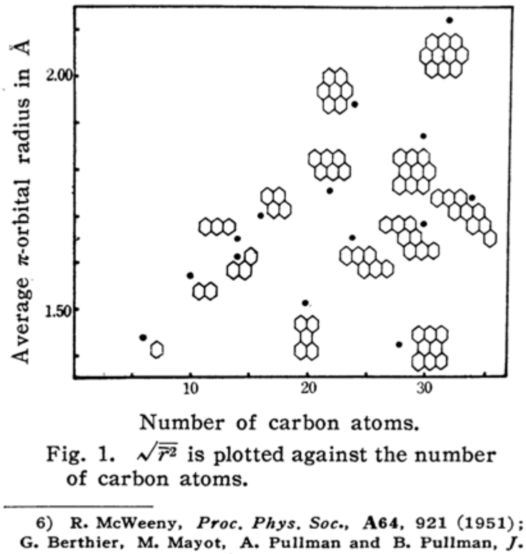

Fig. 1. $\sqrt{\bar{r}^2}$ is plotted against the number of carbon atoms.

The values of K_1, ΔK and $\sqrt{\bar{r}^2}$ have been estimated in a similar way by the empirical formula for pentacene and other polyacenes. The results are shown in Table I.

TABLE I

	$-\chi_M\cdot10^6$	$-K_1\cdot10^6$	$-\Delta K\cdot10^6$	$\sqrt{\bar{r}^2}$ (Å)
Naphthalene	92.2	57.0	106	1.57
Anthracene	130.3	76.3	162	1.65
Tetracene	168.0	95.6	217	1.69
Pentacene	205.4	114.9	272	1.71

The magnetic anisotropies of single crystals of these compounds have been presented, excepting pentacene, and the observed values are as follows,

Naphthalene[4]	$-K_1\cdot10^6=$ 55.0,	$-\Delta K\cdot10^6=114$
Anthracene[4]	69.2,	183
Tetracene[5b]	108.8,	154

In the case of tetracene, the discrepancy in ΔK is great. However, this does not mean that the correctness of the empirical calculation is destroyed. It is rather unnatural for ΔK of tetracene to be smaller than that of anthracene. The direct measurement of anisotropy of a single crystal does not give necessarily the correct value, because it demands a delicate technique.

From the present results, it is found that from naphthalene to pentacene the increment in ΔK is $-55\cdot10^{-6}$ per benzene ring, this value is equal to ΔK_B, therefore, the diamagnetic anisotropy increases proportionally with the number of benzene rings.

Meanwhile, the molecular orbital calculation for the diamagnetic anisotropies of these compounds have been presented as follows[7].

$\Delta K(\text{naphthalene})/\Delta K_B=2.19(S=0)$, $2.22(S=0.25)$,
$\Delta K(\text{anthracene})/\Delta K_B=3.45(S=0)$, $3.53(S=0.25)$,
$\Delta K(\text{tetracene})/\Delta K_B=4.75(S=0)$, $4.88(S=0.25)$,
$\Delta K(\text{pentacene})/\Delta K_B=6.06(S=0)$, $6.26(S=0.25)$

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[6] R. McWeeny, *Proc. Phys. Soc.*, **A64**, 921 (1951); G. Berthier, M. Mayot, A. Pullman and B. Pullman, *J. phys. radium.*, **13**, 15 (1952).

[7] R. McWeeny, *Pro. Phys. Soc.*, **A65**, 839 (1952).

The calculated values are again greater than the observed ones, and the discrepancy tends to be high the larger the molecule is.

The mole susceptibility of pentacene was presented before, that is, $-172\cdot10^{-6}$ by Müller[8] and $-183\cdot10^{-6}$ by Pacault[9]. These values are remarkably smaller than the presumed value from the number of benzene rings in this molecule. In consequence, it has been frequently assumed that in polyacene series the localization of π-electrons or even a paramagnetic contribution could take place when the molecule becomes larger. But it reveals, from the present results, that this is not the case. The diamagnetic anisotropy increases proportionally with the number of benzene rings, and this means, in the case of polyacene series, that the effective π-orbital radius becomes constant regardless of the number of aromatic rings, since the increment in the number of π-electrons is four per one benzene ring.

We are grateful to Dr. E. Clar who kindly provided us with his samples of coronene and pentacene. Violanthrene and anthracene were prepared by Mr. J. Aoki to whom our hearty thanks are due.

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[8] E. Müller and I. Müller-Rodloff, *Ann.*, 517, 134 (1935).

[9] A. Pacault and Ch. Marshalk, *Bull. soc. chim. France*, 19, 141 (1952).